ELASTOMERS IN OSCILLATORY UNIAXIAL EXTENSION

C. Dessi$^1$, D. Vlassopoulos$^1$
A.J. Giacomin$^{2,3,*}$, C. Saengow$^{2,4}$

$^1$F.O.R.T.H., Institute of Electronic Structure and Laser
71110 Heraklion, Crete, GREECE

$^2$Chemical Engineering Department
Polymers Research Group

$^3$Mechanical and Materials Engineering Department
Queen’s University
Kingston, ON K7L 3N6 CANADA

$^4$Mechanical and Aerospace Engineering Department
Polymer Research Center
King Mongkut’s University of Technology North Bangkok
Bangkok, THAILAND 10800

This report is circulated to persons believed to have an active interest in the subject matter; it is intended to furnish rapid communication and to stimulate comment, including corrections of possible errors.

*Corresponding author (giacomin@queensu.ca)

QU-CHEE-PRG-TR--2016-21
ELASTOMERS IN OSCILLATORY UNIAXIAL EXTENSION

C. Dessi\textsuperscript{1}, D. Vlassopoulos\textsuperscript{1}, A.J. Giacomin\textsuperscript{2,3,*}, C. Saengow\textsuperscript{2,4}

\textsuperscript{1} F.O.R.T.H., Institute of Electronic Structure and Laser
71110 Heraklion, Crete, GREECE

\textsuperscript{2} Chemical Engineering Department
Polymers Research Group

\textsuperscript{3} Mechanical and Materials Engineering Department
Queen’s University
Kingston, ON K7L 3N6 CANADA

\textsuperscript{4} Mechanical and Aerospace Engineering Department
Polymer Research Center
King Mongkut’s University of Technology North Bangkok
Bangkok, THAILAND 10800

ABSTRACT

In this work, we subject elastomers to a fixed pre-stretch in uniaxial extension, $\varepsilon_p$, upon which a large-amplitude, $\varepsilon_0$, oscillatory uniaxial extensional (LAOE) deformation is superposed. We find that if both $\varepsilon_p$ and $\varepsilon_0$ are large enough, the stress responds with a rich set of higher harmonics, both even and odd. We further find the Lissajous-Bowditch plots of our measured stress responses versus uniaxial strain to be without two-fold symmetry, and specifically, to be shaped like convex bananas. Our new continuum uniaxial model for this behavior combines a new nonlinear spring, in parallel with a Newtonian dashpot, and we call this the Voigt model with strain-hardening. We consider this three-parameter (Young’s modulus, viscosity and strain-hardening coefficient) model to be the simplest relevant one for the observed convex bananas. We fit the parameters to our both uniaxial elongation measurements at constant extension rate, and then to our LAOE measurements. We develop analytical expressions for the Fourier components of the stress response, parts both in-phase and out-of-phase with the extensional strain, for the zeroth, first, second and third harmonics. We find that the part of the second harmonic that is out-of-phase with the strain must be negative for proper banana convexity.

*Corresponding author (giacomin@queensu.ca)
# CONTENTS

I. INTRODUCTION .................................................................................................................. 5

II. BANANA MODELING .......................................................................................................... 7
   a. Treloar Spring .................................................................................................................. 7
   b. Strain-Hardening Spring ............................................................................................... 8
   c. Strain-Hardening Spring in Voigt Element ................................................................. 10
      i. Steady Uniaxial Extension ....................................................................................... 10
      ii. Large-Amplitude Oscillatory Extension .................................................................. 10

III. EXPERIMENTS .................................................................................................................. 12

IV. RESULTS ............................................................................................................................. 13

V. WORKED EXAMPLES: USING THE FOURIER COEFFICIENTS .................................... 14

VI. CONCLUSION ...................................................................................................................... 14

VII. ACKNOWLEDGMENT ...................................................................................................... 15

VIII. APPENDICES .................................................................................................................. 15
   a. Fourier Analysis of Strain Hardening Spring Voigt Element ..................................... 15
   b. Viscous Dissipation ....................................................................................................... 17

IX. REFERENCES ..................................................................................................................... 32
slip either under high $\dot{\varepsilon}$ or $\dot{\varepsilon}$, one extra tape is used at each sample end.
Figure 12: Fourier responses of strain-hardening spring in Voigt element (cyan), Eq. (34), for \( \varepsilon_0 = 0.3 \), \( \varepsilon_p = 0.5 \) and \( \omega = \frac{\pi}{10}, \frac{2\pi}{10}, 2\pi \) rad/s, and the fitting parameters \( E = 25.1 \) MPa, \( \eta = 6.68 \) MPa s and \( h = 1.67 \) [Eq. (35) with Eqs. (39),(40) and (42)-(44)].
I. INTRODUCTION

Rubbers and elastomers are often subject in service to an oscillatory extensional deformation superposed on a steady one. Tires, for instance, are first inflated (steady pre-stretch) and then roll (superposed oscillatory deformation) [1,2,3]. Similarly, fan or conveyor belts are also exposed to an oscillatory extensional deformation superposed on their pre-stretch. For filled elastomers, large-amplitude oscillatory shear testing (without pre-shear) is commonly used to detect filler aggregation (see § 3. of [4]; [5,6,7]). In contrast to previous large-amplitude oscillatory experiments on solid polymers [8], filled elastomers [4,5], melts [9,10], insect muscle [11] all conducted in shear (and without pre-shear), this work focuses on large-amplitude oscillatory extension (with pre-stretch).

Oscillatory extension has not been used often. One reason is that its experimental realization is not trivial. A careful experimental study with soft polymeric networks had been reported by Hassager and co-workers using the filament stretching rheometer (with which uniaxial extension can be thoroughly controlled) [23] and later analyzed by Rasmussen et al. [10]. Yet, large-amplitude oscillatory extension (LAOE) testing is both interesting scientifically and useful technologically [12]. In particular, repeated LAOE cycles can provide a good quantitative measure of the tested material’s softening performance during processing. Mullins [13,14,15] discovered this and so this softening in oscillatory extension is called the Mullins effect, and this test for softening is used routinely [16,17]. However, we find a mathematical analysis of LAOE to be both challenging and wanting.

This work is a first attempt in this direction. We subject elastomers to a fixed pre-stretch in uniaxial extension, \( \varepsilon_p \), upon which a large-amplitude, \( \varepsilon_0 \), oscillatory uniaxial extensional deformation is superposed:

\[
\varepsilon = \varepsilon_p + \varepsilon_0 \sin \omega t
\]

Figure 1 illustrates this deformation, for which nomenclature has yet to be standardized [18]. In this paper, dimensional variables are defined in Table I, and dimensionless variables or groups, in Table II. If both \( \varepsilon_p \) and \( \varepsilon_0 \) are large enough, the stress responds with a rich set of higher harmonics, both even and odd:

\[
\tau_{xx} = \frac{\tau''_0}{2} + \sum_{n=1,1}^{\infty} \tau'_n \sin \omega t + \tau''_n \cos \omega t
\]

\[
\equiv \varepsilon_0 \sum_{n=0,1}^{\infty} E'_n \sin \omega t + E''_n \cos \omega t
\]

and we make these higher harmonics the focus of this paper.

We examine the Lissajous-Bowditch plots [19] of our measured stress responses versus the uniaxial strain. Our new continuum uniaxial model for these loops combines a new nonlinear spring in parallel with a Newtonian dashpot, and we call this the Voigt model with strain-hardening spring (see Subsection II.c, Figure 5). We consider this three-parameter model to be the simplest relevant one for the observed convex bananas. By convex banana, we mean that both the upper and lower branches of the \( \tau_{xx} - \varepsilon \) loop are convex. By
convex branch, we mean that all of the branch’s chords lie above the branch. We fit our three strain-hardening rubber model parameters (Young’s modulus, viscosity and strain-hardening coefficient) to our uniaxial elongation measurements at constant strain rate. We construct fingerprints to deepen our understanding of this bananas convexity. We calculate the energy dissipated per unit volume over each cycle:

$$\oint \tau_{xx} \, d\varepsilon = \pi \varepsilon_0^2 \varepsilon^\prime$$

(4)

which we derive in Appendix VIII.b.

We develop analytical expressions for the Fourier components of the stress response, parts both in-phase and out-of-phase with the extensional strain, for the zeroth, first, second and third harmonics. We find that the part of the second harmonic that is out-of-phase part with the strain must be negative for proper banana convexity. We can illustrate this by first adimensionalizing Eq. (2), and truncating it after the second harmonic, as:

$$\frac{\tau_{xx} - \tau_0''}{2 \tau_1'} = \frac{2 \tau_{xx} - \tau_0''}{2 \tau_1'} = \sin \omega t + \frac{\tau_1''}{\tau_1'} \cos \omega t + \frac{\tau_1'}{\tau_1'} \sin 2\omega t + \frac{\tau_1''}{\tau_1'} \cos 2\omega t$$

(5)

Since the harmonics higher than the second, is typically less than 2% of the first harmonic (see p. 58 of [2],[20,21,22]), we therefore assumed that the stress response is to be described by the first three harmonics, which are the zeroth, first and second. Figure 2 illustrates the effects of these harmonic coefficients, $$\tau_{xx}''/\tau_1,'' \tau_{xx}'/\tau_1'$$ and $$\tau_{xx}'''/\tau_1'''$$ on the loop shapes. Figure 3 compares the following two special cases of Eq. (5):

$$\frac{2 \tau_{xx} - \tau_0''}{2 \tau_1'} = \sin \omega t + \frac{1}{5} \cos \omega t + \frac{1}{20} \sin 2\omega t + \frac{1}{5} \cos 2\omega t$$

(6)

$$\frac{2 \tau_{xx} - \tau_0''}{2 \tau_1'} = \sin \omega t + \frac{1}{5} \cos \omega t + \frac{1}{20} \sin 2\omega t - \frac{1}{5} \cos 2\omega t$$

(7)

which differ only by the sign of $$\tau_{xx}''$$, that is, by the sign of the part of the second harmonic that is in-phase with $$\cos 2\omega t$$. To explain convex bananas, we seek a constitutive equation for which:

$$\tau_{xx}'' < 0$$

(8)

which is a sufficient condition for banana convexity.

For our experiments on elastomers, we follow the following protocol. First, the engineering strain, $$\varepsilon$$, is raised to the pre-stretch value, $$\varepsilon_p$$, at a constant extensional strain rate:

$$\varepsilon \equiv \left(t - t_0\right) \dot{\varepsilon}_p; \quad \varepsilon \leq \varepsilon_p$$

(9)

then, an oscillation is imposed (never to exceed $$\varepsilon_p$$ and never to fall below zero):

$$\varepsilon = \varepsilon_p + \varepsilon_0 \sin \omega t; \quad \varepsilon_0 < \varepsilon_p; \quad \varepsilon > 0$$

(10)

and thus,

$$\dot{\varepsilon} \equiv \frac{d\varepsilon}{dt} = \dot{\varepsilon}_0 \cos \omega t$$

(11)
where $\dot{\varepsilon}_0 \equiv \varepsilon_0 \omega$. By engineering strain, we mean the change in length per unit initial length (see TABLE V. of [18]). Figure 4 illustrates the specific protocol ($\dot{\varepsilon}_p = 0.01 \text{s}^{-1}$, $\varepsilon_p = 0.5$ and $\varepsilon_0 = 0.5$, see Subsection 5.2 of [23]) used in Figure 10. Eq. (10) can be normalized as:

$$\vec{\varepsilon} \equiv \frac{\varepsilon}{\varepsilon_p} = 1 + \frac{\varepsilon_0}{\varepsilon_p} \sin \omega t \equiv 1 + \varepsilon \sin \omega t = 1 + \varepsilon \sin \tau$$

where $\tau \equiv t/\lambda$ and $\lambda \equiv \eta/E$ are the dimensionless and the characteristic time, and where the Deborah number is given by:

$$\text{De} \equiv \lambda \omega$$

which we will use extensively below in Subsection II.c.ii.

Eqs. (9) and (10) differ from the experimental protocols used for polymer melts, also called large-amplitude oscillatory extension. Specifically, our protocol [Eqs. (9) and (10)] differs from Eq. (4) of [9], specified in term of Hencky strain:

$$\varepsilon_H(t) \equiv \ln(1 + \varepsilon) = \Lambda_0 [1 - \cos \omega t]$$  \hspace{1cm} (14)

and Eq. (3) of [10], as:

$$\varepsilon_H(t) = \dot{\Lambda}_s t + \Lambda_0[1 - \cos \omega t]$$  \hspace{1cm} (15)

where $\Lambda_0$ is the Hencky strain amplitude and $\dot{\Lambda}_s$ is the steady Hencky strain rate. Eq. (15) thus reduces to Eq. (14) when no steady extension is superposed ($\dot{\Lambda}_s = 0$). Our protocol [Eqs. (9) and (10)] also differs from oscillatory extension experiments on insect muscle (see abscissa of Figure 1. of [11]) for which Eq. (1) has been used, without pre-stretch ($\varepsilon_p = 0$).

II. BANANA MODELING

In this paper, we seek a model to, at least qualitatively, describe the behaviors of elastomers in large-amplitude oscillatory extension superposed upon a steady uniaxial extension [see Eqs. (9) and (10)]. To accomplish this, we first develop our model from the classic model for elastomers (Subsection II.a) to describe, quantitatively, elastomer behavior in uniaxial extension at vanishingly small, constant extension rate (Subsection II.b). We then extend the model to include rate sensitivity for steady uniaxial extension (Subsection II.c.i), and finally, we evaluate our new model in large-amplitude oscillatory extension (Subsection II.c.ii).

a. Treloar Spring

Treating each network strand as an entropic spring, Treloar arrives at the constitutive equation for a simple rubber. His model in uniaxial extension at vanishingly, small constant extension rate (see Eq. (5.3) of [24]; Eq. (3) of [25]) is:
\[ \tau_{xx} = \frac{E}{3} \left( \alpha - \frac{1}{\alpha^2} \right) \]  

(16)

where \( \alpha \) is the extension ratio, the ratio of extended length to initial length. Behavior conforming to Eq. (16) is called rubber elasticity. We can deepen our understanding of Eq. (16) by rewriting it as:

\[ \tau_{xx} = E \left( \alpha - 1 - \frac{1-3\alpha^2 + 2\alpha^3}{3\alpha^2} \right) \]

(17)

\[ = E \left( \alpha - 1 \right) + \frac{1-3\alpha^2 + 2\alpha^3}{-3\alpha^2} \]

where the bracketed [blue] term is the linear elastic contribution, and the braced [green], the nonlinear. This negative braced term contributes concavity (see inset of Figure 6). Now the extensional strain is given by:

\[ \varepsilon \equiv 1 - \alpha \]

so that:

\[ \tau_{xx} = E \left[ \varepsilon \right] + \frac{1 + \frac{1}{2} \varepsilon}{(1 + \varepsilon)^2} \varepsilon^2 \]

(19)

and so that:

\[ \frac{d\tau_{xx}}{d\varepsilon} = E \left[ 1 \right] + \frac{2 + 2\varepsilon + \frac{1}{2} \varepsilon^2}{(1+\varepsilon)^3} \varepsilon \]

(20)

and so, for the initial slope of \( \tau_{xx} (\varepsilon) \):

\[ \lim_{\varepsilon \to 0} \frac{d\tau_{xx}}{d\varepsilon} = E \]

(21)

which is Young’s modulus. Adimensionalizing and rewriting Eq. (19) gives:

\[ \bar{\tau} \equiv \frac{\tau_{xx}}{E} = \left[ \varepsilon \right] + \frac{1 + \frac{1}{2} \varepsilon}{(1+\varepsilon)^2} \varepsilon^2 \]

(22)

Figure 6 illustrates the static behavior of Eq. (22) and compares it with the classic rubber data of Treloar (see FIG. 5.4 of [24]; Fig. 2 of [25]). We see that the nonlinear term in Eq. (19) imparts concavity to the \( \tau_{xx} - \varepsilon \) curve. However, this concavity is only observed near the origin, and \( \tau_{xx} \) then inflects at \( \varepsilon_i = \frac{1}{2} \).

b. Strain-Hardening Spring

In this subsection, we introduce a power-law term \textit{ad hoc} to Eq. (19) to account for the observed inflection in the static behavior of a rubber (see data in Figure 6). Specifically, to fit the data from FIG. 5.4 of [24] (or FIG. 2 of [25]), we propose the still purely elastic model:
\[ \tau_{xx} = E \left[ \epsilon + \frac{1 + \frac{2}{3} \epsilon}{(1 + \epsilon)^2} \epsilon^2 \right] + \left[ h \epsilon^4 \right] \]  
\[ \text{with } \epsilon \text{ raised to the fourth power.} \]

The slot-bracketed term in Eq. (23) fits the observed strain-hardening, and we thus call \( h \) the strain-hardening coefficient. This slot-bracketed term contributes the inflection (see inset of Figure 6). Differentiating Eq. (23) once gives:

\[ \frac{d \tau_{xx}}{d \epsilon} = E \left[ 1 + \frac{2 + 2 \epsilon + \frac{2}{3} \epsilon^2}{(1 + \epsilon)^3} \epsilon \right] + \left[ 4 h \epsilon^3 \right] \]  
\[ \text{and so gives the initial slope, } \lim_{\epsilon \to 0} \left[ \frac{d \tau_{xx}}{d \epsilon} \right], \text{ of Young’s modulus as it should,} \]

and then twice gives:

\[ \frac{d^2 \tau_{xx}}{d \epsilon^2} = E \left\{ -2 \frac{1}{(1 + \epsilon)^4} \right\} + \left[ 12 h \epsilon^2 \right] \]  
\[ \text{Setting this to zero:} \]

\[ 0 = -\frac{6}{(1 + \epsilon_i)^4} + 12 h \epsilon_i^2 \]  
\[ \text{then solve for } \epsilon_i, \text{ gives:} \]

\[ \epsilon_i = \frac{\ddot{\epsilon}}{6} + \frac{2}{3} (\dddot{\epsilon}^{-1} - 1) \]  
\[ \text{where:} \]

\[ \ddot{\epsilon} = \left( 8 + 54 \sqrt{\frac{2}{h} + 6 \sqrt{6 \sqrt{\frac{2}{h} + \frac{27}{h}}}} \right)^{1/3} \]  
\[ \text{is the inflection strain. Substituting Eq. (27), into Eq. (23) gives:} \]

\[ \tau_i = E \left\{ \left[ \frac{\ddot{\epsilon}}{6} + \frac{2}{3} (\dddot{\epsilon}^{-1} - 1) \right] + \frac{1 + \frac{2}{3} \ddot{\epsilon} + \frac{2}{3} (\dddot{\epsilon}^{-1} - 1)}{-\left[ 1 + \frac{2}{3} \ddot{\epsilon} + \frac{2}{3} (\dddot{\epsilon}^{-1} - 1) \right]^2} \left( \frac{\ddot{\epsilon}}{6} + \frac{2}{3} (\dddot{\epsilon}^{-1} - 1) \right)^2 \right\} \]  
\[ + \left[ h \left( \frac{\ddot{\epsilon}}{6} + \frac{2}{3} (\dddot{\epsilon}^{-1} - 1) \right)^4 \right] \]  
\[ \text{the corresponding inflection stress. Figure 7 illustrates the strain-hardening coefficient, } h, \text{ as a function of inflection strain. Adimensionalizing Eq. (23) gives:} \]

\[ \dddot{\epsilon} \equiv \frac{\tau_{xx}}{E} = \frac{1}{3} \left( 1 + \epsilon - \frac{1}{(1 + \epsilon)^2} + h \epsilon^4 \right) \]  
\[ \text{as it should. Figure 6 illustrates the static behavior of Eq. (30).} \]
c. Strain-Hardening Spring in Voigt Element

To incorporate viscous dissipation, we add one Newtonian dashpot in parallel with the strain-hardening spring of Subsection II.b. This dashpot thus imparts area to the \( \tau_{xx} - \varepsilon \) loops, an essential feature of the measured behavior.

Following Fig. 1.4 and Eq. (6) of [26]:

\[
\tau_{xx} = E \left[ \varepsilon \right] + \left\{ \frac{1 + \frac{2}{3} \varepsilon}{(1 + \varepsilon)^2} \varepsilon^2 \right\} + \left[ h \varepsilon^4 \right] + \eta \dot{\varepsilon} \tag{31}
\]

which can be adimensionalized to get:

\[
\bar{\tau} \equiv \frac{\tau_{xx}}{E} = \left[ \varepsilon \right] + \left\{ \frac{1 + \frac{2}{3} \varepsilon}{(1 + \varepsilon)^2} \varepsilon^2 \right\} + \left[ h \varepsilon^4 \right] + \lambda_s \dot{\varepsilon} \tag{32}
\]

Eqs. (31) [or (32)] is our new constitutive equation for uniaxial extension. Eq. (32) is thus the first main result of this paper.

For the special case \( \eta = 0 \), Eq. (31) [or (32)] reduces to Eq. (23) in Subsection II.b above for the strain-hardening spring, and for \( h = \eta = 0 \), to Eq. (17) in Subsection II.a for the Treloar spring, as they should.

i. Steady Uniaxial Extension

For uniaxial extension at constant extension rate, \( \dot{\varepsilon} = \dot{\varepsilon}_s \), Eq. (32) yields:

\[
\bar{\tau} = \bar{\tau}_{xx} = \left[ \varepsilon \right] + \left\{ \frac{1 + \frac{2}{3} \varepsilon}{(1 + \varepsilon)^2} \varepsilon^2 \right\} + \left[ h \varepsilon^4 \right] + \lambda_s \dot{\varepsilon}_s \tag{33}
\]

where \( \lambda_s \) is the characteristic time in steady uniaxial extension. Figure 8 illustrates the behavior of Eq. (33) in steady uniaxial extension.

ii. Large-Amplitude Oscillatory Extension

For large-amplitude oscillatory extension (LAOE), we substitute Eqs. (10) and (11) into Eq. (33) to get:

\[
\bar{\tau} = \left[ \varepsilon_p + \varepsilon_0 \sin \omega t \right] + \left\{ \frac{1 + \frac{2}{3} \varepsilon_p + \varepsilon_0 \sin \omega t}{(1 + \varepsilon_p + \varepsilon_0 \sin \omega t)^2} \left( \varepsilon_p + \varepsilon_0 \sin \omega t \right)^2 \right\}
\]

\[
+ \left[ h \left( \varepsilon_p + \varepsilon_0 \sin \omega t \right)^4 \right] + \varepsilon_0 \text{Decos} \omega t \tag{34}
\]

Rewriting Eq. (34) as a Fourier series gives:

\[
\bar{\tau} = \frac{\varepsilon_0''}{2} + \sum_{n=1,2} \varepsilon_n' \sin n \omega t \text{Dec} \tau + \varepsilon_0'' + \sum_{n=2,2} \varepsilon_n'' \cos n \omega t \text{Dec} \tau \tag{35}
\]
since:
\[
\mathbb{E}_n' = 0; \quad n = 2, 4, 6\ldots
\] (36)
and since:
\[
\mathbb{E}_n'' = 0; \quad n = 3, 5, 7\ldots
\] (37)

The Fourier coefficients of \( \sin n\eta \) in Eq. (35) are given by:
\[
\mathbb{E}_n' = \frac{1}{\pi} \int_0^{2\pi} \sin n\eta \, d\eta
\] (38)
so that for the first harmonic:
\[
\mathbb{E}_1' = [\varepsilon_0] + \left\{ \frac{2}{3} \varepsilon_0 \left( \left(1 + \varepsilon_p^2\right) - \varepsilon_0^2 \right)^{-\frac{3}{2}} \right\} + \left[ h \varepsilon_p \left(4\varepsilon_p^2 + 3\varepsilon_0^2\right) \right]
\] (39)
and, for the third:
\[
\mathbb{E}_3' = \left\{ \frac{2}{3} \varepsilon_0 \right\} \left[ \frac{8 \left(1 + \varepsilon_p^2\right)^4 - 12 \left(1 + \varepsilon_p^2\right) \varepsilon_0^2 + 3 \varepsilon_0^4}{\left(1 + \varepsilon_p^2 - \varepsilon_0^2\right)^{3/2}} - 8 \left(1 + \varepsilon_p^2\right) \right] + \left[ -h \varepsilon_p^2 \right]
\] (40)

The Fourier coefficients of \( \cos n\eta \) in Eq. (35) are given by:
\[
\mathbb{E}_n'' = \frac{1}{\pi} \int_0^{2\pi} \cos n\eta \, d\eta
\] (41)
so that for the zeroth harmonic:
\[
\mathbb{E}_0'' = \left[ 2 \left(1 + \varepsilon_p\right) \right] + \left\{ \frac{-2}{3} \left(1 + \varepsilon_p\right) \left(2 + \left(1 + \varepsilon_p^2 - \varepsilon_0^2\right)^{-3/2}\right) \right\} + \left[ h \left(2\varepsilon_p^4 + 6\varepsilon_p^2 + \frac{3}{4} \varepsilon_0^4\right) \right]
\] (42)
and, for the first:
\[
\mathbb{E}_1'' = \varepsilon_p \eta
\] (43)
and, finally, for the second:
\[
\mathbb{E}_2'' = \left\{ \frac{2}{3} \varepsilon_0 \right\} \left[ \frac{-2 \left(1 + \varepsilon_p^3\right) - 3 \left(1 + \varepsilon_p\right) \varepsilon_0^2}{\left(1 + \varepsilon_p^2 - \varepsilon_0^2\right)^{3/2}}\right] + \left[ -h \varepsilon_p^2 \left(3\varepsilon_p^2 + \frac{\varepsilon_0^2}{2}\right) \right]
\] (44)

From Eqs. (39)-(40) and (42)-(44), we learn that only \( \mathbb{E}_1'' \) is affected by the Deborah number and, thus only \( \mathbb{E}_1'' \) depends on the test frequency, \( \omega \). From which we learn that, for our model, increasing \( \omega \) increases the viscous dissipation, and affects nothing else. Our expressions for the Fourier coefficients of the stress response, Eqs. (39)-(40) and (42)-(44), are the second main result of this paper. For the special case of \( \eta = 0 \), Eqs. (39)-(40) and (42)-(44) reduce to the corresponding Fourier coefficients for the strain-hardening spring [Eq. (23) in Subsection II.b above]. For the special case of \( h = \eta = 0 \), Eqs. (39)-(40) and (42)-(44) reduce to the corresponding Fourier coefficients for the Treloar spring [Eq. (17) in Subsection II.a above].

Substituting Eq. (44) into Eq. (8) gives:
\[ 8\left(1 + \varepsilon_p\right)^2 - 4\varepsilon_0^2 + \left[-8\left(1 + \varepsilon_p\right) - 3h\varepsilon_0^4\left(\varepsilon_0^2 + 6\varepsilon_p^2\right)\right]\sqrt{(1 + \varepsilon_p)^2 - \varepsilon_0^2} < 0 \]  
the sufficient condition for banana convexity. Eq. (45) is always satisfied for our model [Eq. (31)]. In other words, our new model always predicts correct banana convexity.

III. EXPERIMENTS

We study an experimental grade of vulcanized styrene-butadiene rubber (SBR) random copolymer filled with silica particles that are functionalized with silane. This elastomer is filled with 5.3% by volume of silica particles, corresponding to 10 parts per hundred by weight. Using differential scanning calorimetry, we measured \( T_g = -21^\circ \text{C} \) (see Subsection 2.5 of [23]). We used rectangular samples of length 15-17 mm (free length of 12.7 mm), width 0.4 mm and thickness 0.7 mm shown in Figure 11.

For this material, we have performed uniaxial extension in (1) at constant extension rate (Eq. (9) with \( t_0 = 0 \) and \( \dot{\varepsilon}_p = \dot{\varepsilon} = \frac{1}{100}, \frac{1}{10}, 1\text{s}^{-1} \)), and (2) large-amplitude oscillation [Eqs. (9) and (10)], using the Sentmanat extensional rheometer (SER) fixture (Xpansion Instrument, LLC, Tallmadge, OH) [27,28] mounted on an ARES 2k FRTN1 strain-controlled rheometer equipped with a force rebalance transducer (TA Instruments, New Castle, DE) photographed in Figure 11. The convection oven temperature is controlled to \( T = 25 \pm 0.1^\circ \text{C} \). To avoid grip-slip on the wind-up drums of the SER, we covered the surface of the drums with double-sided tape and extra tapes at each end of each specimen (Figure 11).

Achieving nearly perfect uniaxial extension is challenging. During our stretching experiment, we thus use a camera to monitor the sample shape, and thus to determine the imperfections of the experiment [23,29]. One possible imperfection is the detachment of part of the sample from the rotating drums, during the second half of a period, may lead to slight departures from uniformly uniaxial extension. For the data reported here, we managed to achieve nearly perfect uniaxial extension (and reproducible results) by (1) applying a pre-stretch, (2) keeping our frequencies down, and (3) by strongly attaching the sample to the drums. We are thus convinced that the observed nonlinear responses reported below are not artifacts of experimental imperfections. Specifically, the effects leading to the banana-shaped Lissajous-Bowditch plots (consistent with literature observations see [13,15,17]), we are thus convinced, are property of the material. By extension, the discrepancies with our new model, reported below, are also real.

All LAOE measurements were performed by applying the pre-stretch of \( \varepsilon_0 = 0.5 \) and \( \dot{\varepsilon}_p = 0.01\text{s}^{-1} \) onto which a sinusoidal oscillatory extension of amplitude \( \varepsilon_0 = 0.3 \) is superposed. LAOE Experiments were performed at three frequencies, \( \omega = \frac{\pi}{50}, \frac{\pi}{5} \) and \( 2\pi \text{rad/s} \). For \( \omega = \frac{\pi}{5} \text{rad/s} \), Figure 9 shows that the filled elastomer in LAOE reaches alternance before the third cycle. Since our special Voigt element prediction contains no decaying term, it cannot predict the
(rapid) approach to alternance documented in Figure 9. Between the origin and the black circle (O) in Figure 9, Eq. (9) of our protocol applies, and thereafter, Eq. (10). This black circle indicates small imperfection in strain control at the time of the mode switch, from Eq. (9) \( t < 0 \) to Eq. (10) \( t = 0 \). We report the 49th cycle measurements in Figure 10 to ensure that alternance has been reached.

IV. RESULTS

Throughout this paper, and thus, on the ordinates of Figure 6, Figure 8 and Figure 10, we report the true stress, given by (see Eq. (5.4) of [24]):

\[
\tau_{xx} = \frac{(1 + \varepsilon) F}{A_0}
\]  

(46)

Figure 6 illustrates the fitting of the Treloar spring [Eq. (22) for \( E = 1.17 \text{ MPa} \)] and of our new strain-hardening spring [Eq. (30) for \( E = 1.17 \text{ MPa} \) and \( h = 0.063 \)] to the classic static extension measurements on natural rubber, taken from Treloar’s curve (a) in Fig. 5.4 of [24]. From Figure 6, we find that our new strain-hardening spring [Eqs. (23) or (30)] is adequate, since it provides the right inflection, at the right measured value of the inflection strain, \( \varepsilon_i = 0.5 \).

Figure 8 illustrates the best fit of our new Voigt model with strain-hardening spring [Eq. (33)] to our own steady uniaxial extension measurements on the filled elastomer (see Figure 5.5 of [23]). From Figure 8, we learn that for a fitted value of \( h = 1.67 \), our model agrees well with the measured values, which are all in the convex regime of the elastomer response.

Figure 10 illustrates the best fit of our new Voigt model with strain-hardening spring [Eq. (34)] to our LAOE measurements on the filled elastomer (see red loops in Figure 5.10 of [23]). From Figure 10, we learn that for a fitted value of \( h = 3.33 \), our model agrees well with our loops measured in LAOE. Comparing the \( h = 3.33 \) (Figure 10) obtained for LAOE with the \( h = 1.67 \) (Figure 8) obtained for steady uniaxial extension, we get eight times the \( E \), ten times the \( \eta \) and twice the \( h \) in LAOE versus steady uniaxial extension. We speculate that multiple Voigt elements with strain-hardening springs in parallel would improve the fit in LAOE.

We can deepen our understanding of our results by comparing our LAOE experiments with our own steady uniaxial extension experiments in dimensionless terms. Whereas LAOE involves both Deborah [see Eq. (13)] and Weissenberg:

\[
W_i = \bar{\lambda}_s \dot{\varepsilon}_0 = \varepsilon_0 \eta / E
\]  

(47)

numbers, steady uniaxial extension just involves a Weissenberg number:

\[
W_i = \dot{\lambda}_s \dot{\varepsilon}_s = \dot{\varepsilon}_s \eta / E
\]  

(48)

Furthermore, steady uniaxial extension is not a limiting case of LAOE, and specifically, not the limiting case \( De \to 0 \). This is because whereas steady uniaxial extension has only one controlled parameter \( \dot{\varepsilon}_s \), LAOE is a test with three controlled parameters \( \varepsilon_0, \varepsilon_p \) and \( \omega \). Furthermore, the Weissenberg
number ranges for our steady extensional experiments, 0.02 < Wi < 0.2 (where \( \lambda_s = 0.218 \)) and for our LAOE experiments, 0.05 < Wi < 0.5 (where \( \lambda_L = 0.266 \)) overlap. The Deborah number range for our LAOE experiments is 0.0167 < De < 1.67.

From the top loop in Figure 10, we further find that, at high frequency, our model overpredicts the stress-strain loop area, and thus overpredicts the viscous dissipation.

V. WORKED EXAMPLES: USING THE FOURIER COEFFICIENTS

In this section, we demonstrate the usefulness of our analytical expressions for the Fourier coefficients for our Strain-Hardening Spring in Voigt Element. Substituting the testing parameters \( \varepsilon_0 = 0.3 \), \( \varepsilon_p = 0.5 \) and \( \omega = 2\pi, \frac{2\pi}{10}, \frac{2\pi}{100} \) rad/s, and the fitting values \( E = 25.1 \) MPa, \( \eta = 6.68 \) MPa s and \( h = 3.33 \) into Eqs. (39) and (40) gives:

\[
\begin{align*}
\mathbb{E}_1' & = 0.798, 0.798, 0.798 \quad \text{(49)} \\
\mathbb{E}_3' & = -0.0463, -0.0463, -0.0463 \quad \text{(50)} \\
\text{and then, into Eqs. (42) through (44):} \\
\mathbb{E}_0'' & = 1.57, 1.57, 1.57 \quad \text{(51)} \\
\mathbb{E}_1'' & = 0.501, 0.0501, 0.00502 \quad \text{(52)} \\
\mathbb{E}_2'' & = -0.229, -0.229, -0.229 \quad \text{(53)}
\end{align*}
\]

We then use these moduli to construct the corresponding (cyan) loops in Figure 12. These (cyan) loops are constructed from our analytical expressions for the Fourier coefficients. The expression for these Fourier coefficients [Eqs. (39)-(40) and (42)-(44)] were derived from Eq. (34), the analytical solution for our Voigt model with a strain-hardening spring in LAOE (black) loops. The close agreement between the (cyan) loops and the (black) loops in Figure 12 shows that harmonics higher than the third can be neglected for elastomers in LAOE.

Rewriting our sufficient condition for banana convexity, Eq. (8), as:

\[
\mathbb{E}_2'' < 0 \quad \text{(54)}
\]

and comparing Eqs. (53) with Eq. (54), we see that for all three banana-shaped loops in Figure 10, our sufficient condition for banana convexity is satisfied, as it should.

VI. CONCLUSION

We have studied two types of spring, the Treloar spring and the strain-hardening spring. We find that whereas the Treloar spring always gives concavity, measured elastomer behavior at large extension always involves convexity.
We find that our new strain-hardening spring model [Eq. (23)] imparts convexity, and is adequate for static extension of natural rubber including at large extension (Figure 6).

Our new constitutive model, the Voigt element with strain-hardening spring [Eq. (33)], agrees well with our own steady uniaxial extension measurements on filled elastomer (Figure 8). This new constitutive model can also agrees be fitted to our LAOE measurements on the filled elastomer (Figure 10), though not nearly as well as for steady uniaxial extension. We speculate that multiple Voigt elements with strain-hardening springs in parallel would improve the fit in LAOE.

We evaluate our new constitutive model in both steady uniaxial extension, and in large-amplitude oscillatory extension. For the latter, this new model yields analytical expressions for the dominant (zeroth through the third) Fourier coefficients of the measured stress response [Eqs. (39)-(40) and (42)-(44)]. In Eq. (8), we state the sufficient condition for banana convexity, and our new constitutive model predicts correctly banana convexity. From our WORKED EXAMPLES, we conclude that harmonics higher than the third can be neglected for elastomers in LAOE.

Our new model overpredicts the stress-strain loop area, and thus overpredicts the viscous dissipation at high frequency (top loop, Figure 10). We speculate that the multiple Voigt elements with strain-hardening springs in parallel would address this.

VII. ACKNOWLEDGMENT

This research was undertaken, in part, thanks to funding from the Canada Research Chairs program of the Government of Canada for the Natural Sciences and Engineering Research Council of Canada (NSERC) Tier 1 Canada Research Chair in Rheology. Saengow appreciates the financial support of Rajamangala University of Technology Lanna. Giacomin is indebted to the Faculty of Applied Science and Engineering of Queen’s University at Kingston, for its support through a Research Initiation Grant (RIG). Vlassopoulos and Dessi acknowledge financial support of Greek General Secretariat for Research and Technology (grant Thalis-380238 COVISCO).

We thank Mr. Baptiste Gaumond of the Institut National des Sciences Appliquées de Lyon for his help with Figure 1. We thank Prof. Wilhem of Karlsruhe Institute of Technology for giving the access to ARES G2, and for hosting Dr. Dessi.

VIII. APPENDICES

a. Fourier Analysis of Strain Hardening Spring Voigt Element

In this appendix, we evaluate the integrations in Eqs. (38) and (41). Rewriting Eq. (34):
\[
\tilde{\tau} = [\varepsilon_p + \varepsilon_0 \sin \omega t] + \left\{ \frac{1 - 2\varepsilon_p - 2\varepsilon_0 \sin \omega t}{3} - \frac{1}{3\left(1 + \varepsilon_p + \varepsilon_0 \sin \omega t\right)^2} \right\} + \left[ h \left( \varepsilon_p + \varepsilon_0 \sin \omega t \right)^4 \right] + \varepsilon_0 \cos \omega t
\]

Introducing:
\[
\zeta \equiv 1 + \varepsilon_p
\]

into Eq. (55) gives:
\[
\tilde{\tau} = [\!-1 + \zeta + \varepsilon_0 \sin \omega t] + \left\{ \frac{3 - 2\zeta - 2\varepsilon_0 \sin \omega t}{3} - \frac{1}{3\left(\zeta + \varepsilon_0 \sin \omega t\right)^2} \right\} + \left[ h \left( \!-1 + \zeta + \varepsilon_0 \sin \omega t \right)^4 \right] + \varepsilon_0 \cos \omega t
\]

Substituting Eq. (57) into Eq. (38) gives the coefficients of \(s\) in Eq. (35):
\[
\mathbb{E}_0' = \frac{1}{\pi} \int_0^{2\pi} \left[ \frac{2\varepsilon_0}{3} \left( \frac{1}{\left(\zeta^2 - \varepsilon_0^2\right)^{3/2}} - 1 \right) \right] + \left[ h\varepsilon_0 \left( \zeta - 1 \right) \left( 4 - 8\zeta + 4\zeta^2 + 3\varepsilon_0^4 \right) \right] \sin \pi n \varepsilon_0 \, d\varepsilon_0
\]

so that for the first harmonic:
\[
\mathbb{E}_1' = \left[ \varepsilon_0 \right] + \left\{ \frac{2\varepsilon_0}{3} \left( \frac{1}{\left(\zeta^2 - \varepsilon_0^2\right)^{3/2}} - 1 \right) \right\} + \left[ h\varepsilon_0 \left( \zeta - 1 \right) \left( 4 - 8\zeta + 4\zeta^2 + 3\varepsilon_0^4 \right) \right]
\]

and, for the third:
\[
\mathbb{E}_3' = \left\{ \frac{2}{3\varepsilon_0} \left( \frac{8\zeta^4 - 12\zeta^2 \varepsilon_0^2 + 3\varepsilon_0^4}{\left(\zeta^2 - \varepsilon_0^2\right)^{3/2}} - 8\zeta \right) \right\} + \left[ -h\varepsilon_0^3 \left( \zeta - 1 \right) \right]
\]

Substituting Eq. (57) into Eq. (41) gives the coefficients of \(c\) in Eq. (35):
\[
\mathbb{E}_0'' = \frac{1}{\pi} \int_0^{2\pi} \left[ \frac{3 - 2\zeta - 2\varepsilon_0 \sin \omega t}{3} - \frac{1}{3\left(\zeta + \varepsilon_0 \sin \omega t\right)^2} \right] \cos \pi n \varepsilon_0 \, d\varepsilon_0
\]

so that for the zeroth harmonic:
\[
\mathbb{E}_0'' = \left[ 2\zeta \right] + \left\{ \frac{2}{3} \left( \frac{\zeta}{\left(\zeta^2 - \varepsilon_0^2\right)^{3/2}} + 2\zeta \right) \right\} + \left[ h\left( 2\left( \zeta - 1 \right)^4 + 6\varepsilon_0^2 \left( \zeta - 1 \right)^2 + \frac{3}{4}\varepsilon_0^4 \right) \right]
\]

and for the first:
\[
\mathbb{E}_1'' = \varepsilon_0 \, \text{De}
\]

and, finally, for the second:
\[ \mathbb{E}_2'' = \left( \frac{2}{3\epsilon_0^2} \left[ 2 - \frac{2\zeta^2 - 3\zeta^2\epsilon_0^2}{(\zeta^2 - \epsilon_0^2)^{3/2}} \right] + \frac{1}{\epsilon_0^2} \left[ \frac{3(\zeta - 1)^2 + \epsilon_0^2}{2} \right] \right) \] 

(64)

Substituting Eq. (56) back into Eqs. (58)-(64) gives Eqs. (38)-(44) in Subsection II.c.ii above.

### b. Viscous Dissipation

In this appendix, we derive the viscous dissipation per unit volume per cycle. Substituting Eqs. (3) and (11) into the left side of Eq. (4) gives:

\[
W = \epsilon_0^2 \int_0^\pi \sum_{n=0,1} \left[ E''_n \cos \omega t \cos \omega t + E' \sin \omega t \sin \omega t \right] \cos \omega t \, dt \\
= \epsilon_0^2 \left[ \int_0^\pi E'_0 \cos \omega t \cos \omega t \, dt + \int_0^\pi (E''_1 \cos \omega t + E' \sin \omega t) \cos \omega t \, dt \right] \\
+ \sum_{n=2,1} \left[ \int_0^\pi E''_n \cos \omega t \cos \omega t \, dt + \int_0^\pi E' \sin \omega t \sin \omega t \, dt \right] \\
\]

(65)

Since:

\[
\int_0^\pi \cos \omega t \cos \omega t \, dt = \begin{cases} \pi & n = 1 \\ \frac{n \sin 2n\pi}{n^2 - 1} & n \neq 1 \end{cases} \\
\int_0^\pi \sin \omega t \cos \omega t \, dt = \begin{cases} 0 & n = 1 \\ \frac{2n \sin^2 n\pi}{n^2 - 1} & n \neq 1 \end{cases} \\
\]

(66) \hspace{2cm} (67)

Combining Eqs. (66) and (67) with Eq. (65) gives Eq. (4) of Section I above as it should. Substituting Eq. (43) into Eq. (4) gives our expression for the viscous dissipation per unit volume per cycle for our strain-hardening spring in Voigt element.

For the corresponding analyses for large-amplitude oscillatory shear, see Eq. (68) of 30, Eq. (4.12) of 31, Eq. (11.12) of 32, Eq. (175) of [33,34], Eq. (22) of [35] or see Eq. 10 of [36]. From Eq. (4) of Section I, we learn that harmonics higher than the first cannot contribute to the viscous dissipation per unit volume per cycle. In large-amplitude oscillatory shear, the analog to Eq. (4) of Section I is:

\[
\int \tau_{yx} \, d\gamma = \pi \gamma_0^2 G'' \\
\]

(68)

and this has been closely verified experimentally (see close agreement between last two columns of TABLE II of [37] for a filled melt).
### Table I: Dimensional Variables

<table>
<thead>
<tr>
<th>Test frequency</th>
<th>$t^{-1}$</th>
<th>$\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cartesian coordinate</td>
<td>$L$</td>
<td>$x, y, z$</td>
</tr>
<tr>
<td>Extra stress tensor*</td>
<td>$M/Lt^2$</td>
<td>$\tau$</td>
</tr>
<tr>
<td>Viscous dissipation</td>
<td>$M/Lt^2$</td>
<td>$W$</td>
</tr>
<tr>
<td>Extra stress, $ij$-th component</td>
<td>$M/Lt^2$</td>
<td>$\tau_{ij}$</td>
</tr>
<tr>
<td>Extra stress, $xx$-component, in-phase with strain, $n$-th harmonic</td>
<td>$M/Lt^2$</td>
<td>$\tau'_n$</td>
</tr>
<tr>
<td>Extra stress, $xx$-component, out-of-phase with strain, $n$-th harmonic</td>
<td>$M/Lt^2$</td>
<td>$\tau''_n$</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>$M/Lt^2$</td>
<td>$E$</td>
</tr>
<tr>
<td>Elastic modulus, in-phase with strain, $n$-harmonic</td>
<td>$M/Lt^2$</td>
<td>$E'_n$</td>
</tr>
<tr>
<td>Elastic modulus, out-of-phase with strain, simple shear experiment</td>
<td>$M/Lt^2$</td>
<td>$G''_n$</td>
</tr>
<tr>
<td>Elastic modulus, out-of-phase with strain, $n$-harmonic</td>
<td>$M/Lt^2$</td>
<td>$E''_n$</td>
</tr>
<tr>
<td>Steady shear viscosity</td>
<td>$M/Lt$</td>
<td>$\eta$</td>
</tr>
<tr>
<td>Characteristic time</td>
<td>$t$</td>
<td>$\lambda \equiv \eta/E$</td>
</tr>
<tr>
<td>Characteristic time, LAOE experiment</td>
<td>$t$</td>
<td>$\lambda_L$</td>
</tr>
<tr>
<td>Characteristic time, steady uniaxial extension experiment</td>
<td>$t$</td>
<td>$\lambda_s$</td>
</tr>
<tr>
<td>Extensional strain rate</td>
<td>$t^{-1}$</td>
<td>$\dot{\varepsilon} = d\varepsilon/dt$</td>
</tr>
<tr>
<td>Extensional strain rate, steady extension uniaxial</td>
<td>$t^{-1}$</td>
<td>$\dot{\varepsilon}_s$</td>
</tr>
<tr>
<td>Extensional strain rate, pre-stretch</td>
<td>$t^{-1}$</td>
<td>$\dot{\varepsilon}_p$</td>
</tr>
<tr>
<td>Extensional strain rate amplitude</td>
<td>$t^{-1}$</td>
<td>$\dot{\varepsilon}_0 = \varepsilon_0 \omega$</td>
</tr>
<tr>
<td>Extensional strain rate, Hencky</td>
<td>$t^{-1}$</td>
<td>$\dot{\varepsilon}_{H}$</td>
</tr>
<tr>
<td>Time</td>
<td>$t$</td>
<td>$t$</td>
</tr>
<tr>
<td>Time, initial</td>
<td>$t$</td>
<td>$t_0$</td>
</tr>
<tr>
<td>Hencky strain rate</td>
<td>$t^{-1}$</td>
<td>$\Lambda_0$</td>
</tr>
<tr>
<td>Temperature, glass transition</td>
<td>$T$</td>
<td>$T_g$</td>
</tr>
<tr>
<td>Axial force</td>
<td>$ML/t^2$</td>
<td>$F$</td>
</tr>
<tr>
<td>Initial cross section</td>
<td>$L^2$</td>
<td>$A_0$</td>
</tr>
</tbody>
</table>

Legend: $M$ mass; $L$ length; $t$ time; $T$ temperature

* Where $\tau_{ij}$ is the force exerted in the $j$-th direction on a unit area of fluid surface of constant $x_i$ by fluid in the region lesser $x_i$ on fluid in the region greater $x_i$ [38, 39].
### Table II: Dimensionless Variables and Groups

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extensional strain amplitude</td>
<td>$\varepsilon_0$</td>
</tr>
<tr>
<td>Extensional strain amplitude, normalized</td>
<td>$\varepsilon \equiv \varepsilon_0 / \varepsilon_p$</td>
</tr>
<tr>
<td>Extensional strain</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>Shear strain</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>Shear strain, amplitude</td>
<td>$\gamma_0$</td>
</tr>
<tr>
<td>Extensional strain, normalized</td>
<td>$\bar{\varepsilon}$</td>
</tr>
<tr>
<td>Extensional strain, Hencky</td>
<td>$\varepsilon_H$</td>
</tr>
<tr>
<td>Extensional strain amplitude, Hencky</td>
<td>$\Lambda_0$</td>
</tr>
<tr>
<td>Extensional strain, inflection</td>
<td>$\varepsilon_i$</td>
</tr>
<tr>
<td>Extensional strain, normalized</td>
<td>$\bar{\varepsilon} \equiv \varepsilon / \varepsilon_p$</td>
</tr>
<tr>
<td>Extensional strain, pre-stretch</td>
<td>$\varepsilon_p$</td>
</tr>
<tr>
<td>Extension ratio</td>
<td>$\alpha \equiv 1 - \varepsilon$</td>
</tr>
<tr>
<td>Deborah number</td>
<td>$De \equiv \lambda_L \omega$</td>
</tr>
<tr>
<td>$n$ -th harmonic</td>
<td>$n$</td>
</tr>
<tr>
<td>Time</td>
<td>$\tau \equiv t / \lambda_L$</td>
</tr>
<tr>
<td>Extra stress, $xx$ -component</td>
<td>$\bar{\tau} \equiv \tau_{xx} / E$</td>
</tr>
<tr>
<td>Elastic modulus, in-phase with strain, $n$ -th harmonic</td>
<td>$\beta_n' \equiv E'_n / E$</td>
</tr>
<tr>
<td>Elastic modulus, out-of-phase with strain, $n$ -th harmonic</td>
<td>$\beta_n'' \equiv E''_n / E$</td>
</tr>
<tr>
<td>Variable in Eq. (27)</td>
<td>$i$</td>
</tr>
<tr>
<td>Strain-hardening coefficient</td>
<td>$h$</td>
</tr>
<tr>
<td>Transforming variable in Eq. (56)</td>
<td>$\zeta$</td>
</tr>
<tr>
<td>Weissenberg number, steady uniaxial extension</td>
<td>$Wi_s \equiv \lambda_s \dot{\varepsilon}_s$</td>
</tr>
<tr>
<td>Weissenberg number, LAOE</td>
<td>$Wi_L \equiv \lambda_L \dot{\varepsilon}_0$</td>
</tr>
</tbody>
</table>
Figure 1: Elastomer in large-amplitude oscillatory extension.
Figure 2: Effects of harmonic coefficients on loop shapes [Eq. (5)]. Each triad of $(2\tau_{xx} - \tau_0)/2\tau_1$ versus $(\varepsilon - \varepsilon_p)/\varepsilon_0$ loops is parametrized with $\tau''_1/\tau'_1$. 
Figure 3: Loops from Eq. (6) where $\tau''_2 > 0$ (concave banana) and Eq. (7) where $\tau''_2 < 0$ (convex banana).
Figure 4: Large-amplitude oscillatory extension protocol used for loops in Figures 8 and 9 below. Eqs. (9) and (10) with $t_0 = 0\text{s}$, $\dot{\epsilon}_p = 0.01\text{s}^{-1}$, $\epsilon_p = 0.5$ and $\epsilon_0 = 0.5$. 
Figure 5: Strain-hardening spring in Voigt element.
**Figure 6**: Uniaxial steady static behavior of Treloar spring (red) where $E = 1.17 \text{ MPa}$ [Eq. (22)], and of strain-hardening spring (black) where $E = 1.17 \text{ MPa}$ and $h = 0.0210$ [Eq. (30)]. Measurements (circles) from curve (a) in Fig. 5.4 of [24]. Inset shows the inflection of the blue circles at $\varepsilon = 0.375$.
Figure 7: Inflection strain for strain-hardening spring [Eq. (27) with Eq. (28)].
Figure 8: Convex behaviors in steady uniaxial extension. Solid curves for Voigt element with strain-hardening spring [Eq. (33)] for \( E = 3.12 \) MPa, \( \eta = 0.680 \) MPas and \( h = 1.67 \), and circles are measured for styrene-butadiene random copolymer filled with 5.3% by volume of silica \( (T = 25^\circ C) \). Blue, Green and Red curves and circles are shifted upward by 5, 10 and 15.
Figure 9: Experimental observations of start-up of large-amplitude oscillatory extension where $\varepsilon_0 = 0.3$, $\varepsilon_p = 0.5$, $E = 25.1$ MPa and $\omega = \frac{2}{10} \pi$ rad/s. Blue, red and green cycles are for the first, second and the third cycles. Alternance is reached before the third cycle and then maintained.
Figure 10: Experimental observations on large-amplitude oscillatory extension, where $\varepsilon_0 = 0.3$, $\varepsilon_p = 0.5$ and $\omega = \frac{1}{50} \pi, \frac{2}{10} \pi, 2\pi \text{ rad/s}$, versus response of strain-hardening spring in Voigt element with [Eq. (34)] and its Fourier series [Eq. (35) with Eqs. (39), (40) and (42)-(44)] for $E = 25.1 \text{ MPa}$, $\eta = 6.68 \text{ MPa s}$ and $h = 3.33$. Blue and Red curves and circles are shifted upward by 1 and 2.
Figure 11: Strip specimen loaded in the SER fixture for our filled SBR. To avoid slip either under high $\varepsilon$ or $\dot{\varepsilon}$, one extra tape is used at each sample end.
Figure 12: Fourier responses of strain-hardening spring in Voigt element (cyan), Eq. (34), for $\varepsilon_0 = 0.3$, $\varepsilon_p = 0.5$ and $\omega = \frac{\pi}{100}, \frac{3\pi}{10}, 2\pi$ rad/s, and the fitting parameters $E = 25.1$ MPa, $\eta = 6.68$ MPa s and $h = 1.67$ [Eq. (35) with Eqs. (39),(40) and (42)-(44)].
IX. REFERENCES


